Measurement of Nanoparticles True Volume and Density in the Aerosol Phase

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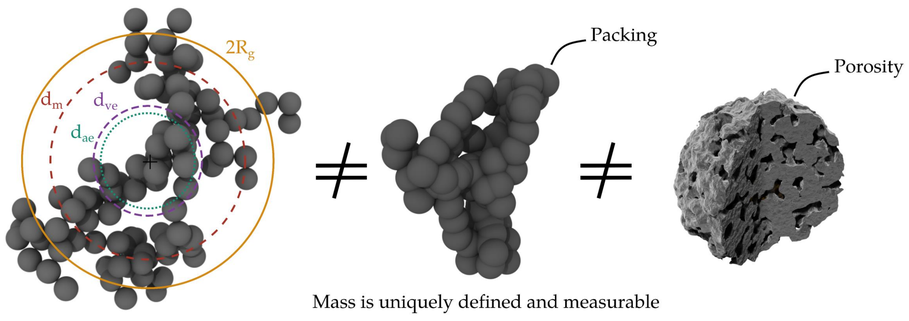
Background and Motivation

- Fundamental aerosol properties such as volume and density are not known[1]
- True volume is crucial to determining density and derived properties, e.g., porosity[2], packing factor[3]



- Material density is usually assumed as a constant value from bulk measurements:
  What about coated, oxidized, or multicomponent (e.g., bimetallic) nanoparticles?
- Precise volume and density are required in numerous applications, such as:
  - Nanotechnology and energy (sensors, plasmonics, catalysis, batteries)
  - Aerosol metrology (realistic metrics, standards, calibration)
  - Environment (black and brown carbon, nanoplastics)
  - Health science (cancer treatment, drug delivery)
  - Industry (powders, coatings)
- **Current gap:** no technique exists for the direct online measurements of volume and density of nanoparticles

Objective: there is an urgent need for developing instruments and techniques that can measure the true properties of nanoparticles as a solid base to further derive secondary properties. This is achieved here by accounting for change in nanoparticles geometry.

Proposition: most nanoparticles can be processed at moderately-high temperatures (**condensation technique**), whereas a minority are temperature sensitive, e.g., plastics (**coagulation technique**)[4]

Condensation Technique

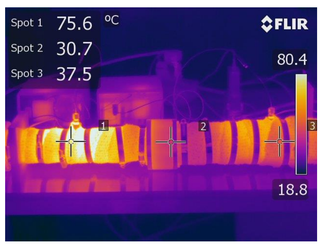


Figure 1: Temperature field (infrared) during warmup.

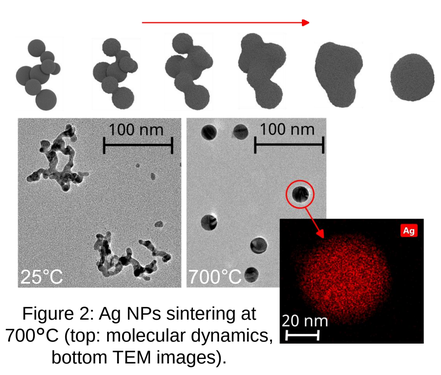


Figure 2: Ag NPs sintering at 700°C (top: molecular dynamics, bottom TEM images).

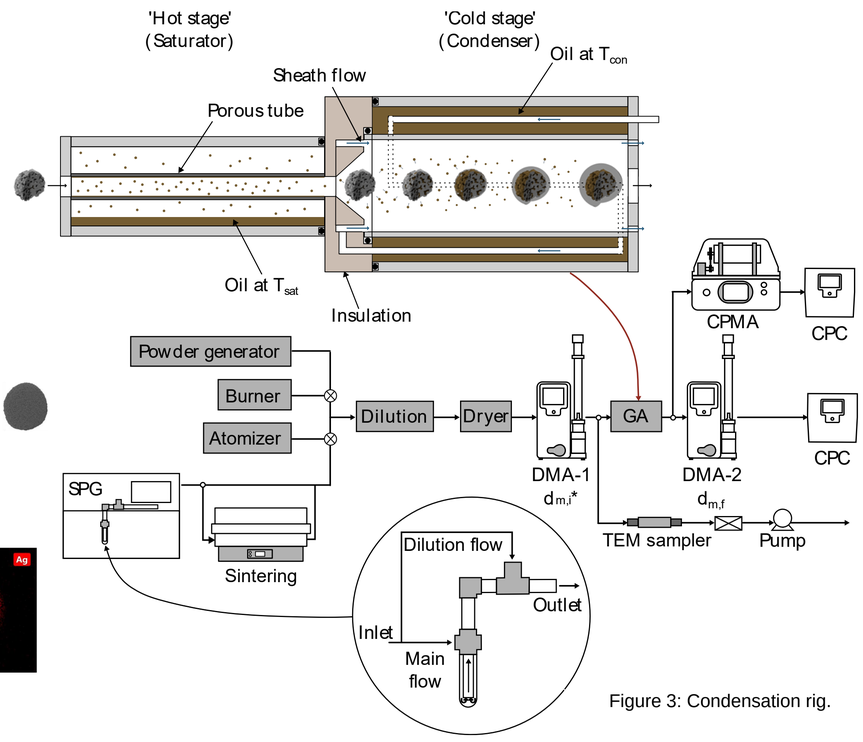
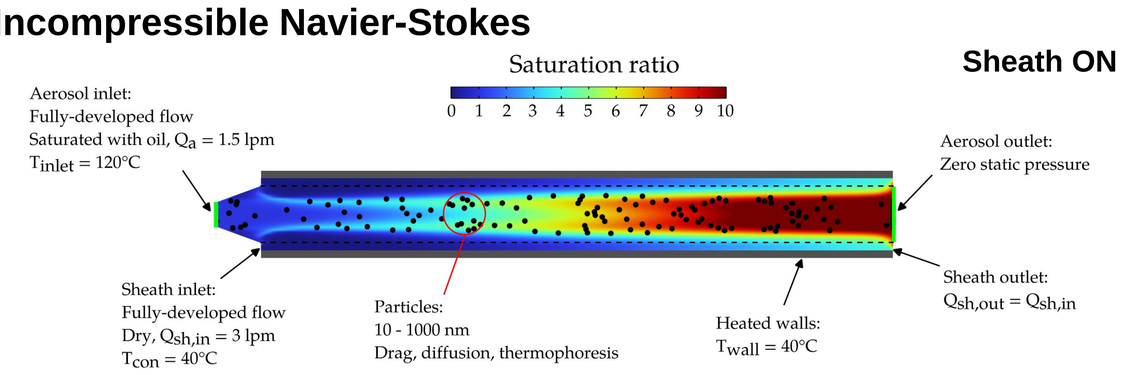


Figure 3: Condensation rig.

- Laminar-flow convective cooling growth apparatus (GA) (Le > 1)
- Wetted porous tube for maximum inlet saturation uniformity
- Temperature-controlled sheath flow to constrain saturation (and particles) along the axis of the condenser
- High temperature saturator and moderately-high temperature condenser
- Working fluids: heavy oils with low vapour pressure

Growth Apparatus Simulation

Incompressible Navier-Stokes



- Vapour and particles transport in the condenser: solutions for heat and mass transfer coupled with Lagrangian particle tracking
- Supersaturation region along the axis with S > 10
- Diverging section to facilitate activation (pressure gradient)
- Residence time for particles ~ 5 s in condenser
- Assuming that all the vapour condenses on the surface of the particles, the final particle size can be estimated, e.g., 50 nm Ag spheres grow up to 300 nm with N = 5.5.10^5 part/cm^3 and T_{sat} = 120°C

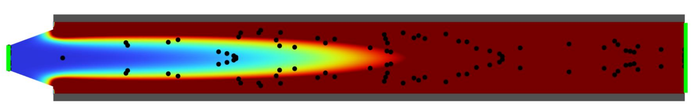


Figure 4: Saturation fields with/without sheath flow (top/bottom)

- Vapour diffuses to the walls while smaller particles are lost
- Poorly-controlled growth (due to large variations in residence time) resulting in broader size distributions

Validation of the Condensation Technique

- Technique was validated using polystyrene nanospheres (PSL) at 220 nm
- Particle growth (mass and mobility diameter) increases monotonically with saturator temperature

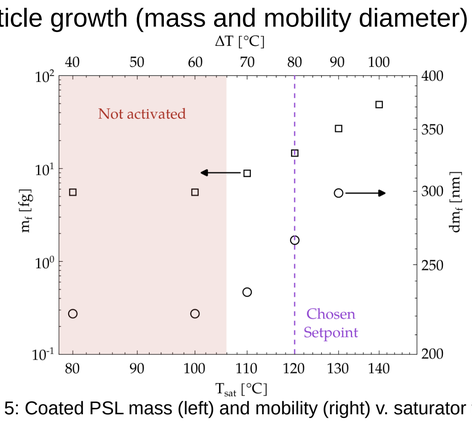


Figure 5: Coated PSL mass (left) and mobility (right) v. saturator temperature.

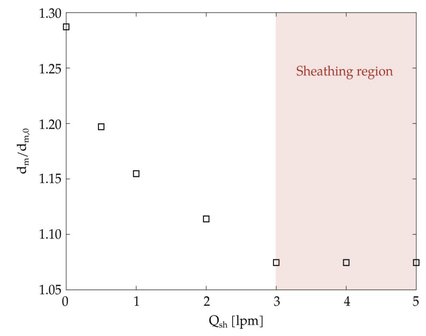


Figure 6: Growth factor v. condenser sheath flow rate.

- Additional sheath flow affects the growth and is crucial for stability:
  Smaller growth, number concentration, and distribution width due to shorter residence time
- This demonstrates the ability of the instrument to cause condensation on hydrophobic polymer surfaces
- Retrieved values for the volume and density differ by 10.9% and 5.2%, respectively, with the PSL manufacturer-derived values

Volume and Density Measurement

Theory and Principles

- (i) Using a very low vapour pressure oil, the coating mass must be conserved
  (ii) A region exists where the particles grow radially, i.e., as spherical droplets

$$\underbrace{(m_f - m_i)}_{\text{change in mass}} = \underbrace{\left(\frac{\pi}{6} d_{m,f}^3 - V_s\right)\rho_c}_{\text{mass of coating}} \quad \text{and} \quad \chi_f = \frac{d_m C_{ve}}{d_{ve} C_m} = 1$$

Processing of Ag Aggregates

- Triple point (P2) separates the multi-stage condensation
- T_{sat} is set in the region [T_{min}, T_{max}]
- Filling mechanisms include
  Ab initio cluster and islands formation (pore adsorption, pendular rings)
  Surface diffusion and film formation v. droplet growth (hydrophobic)

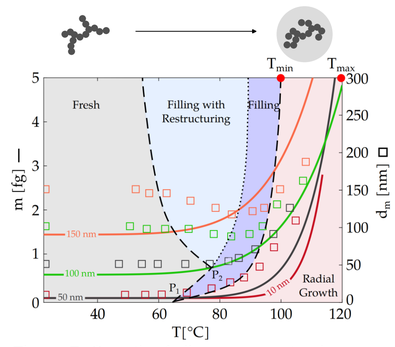


Figure 7: Growth of silver aggregates in mass and mobility with saturator temperature.

Volume/Density of Ag Nanoparticles

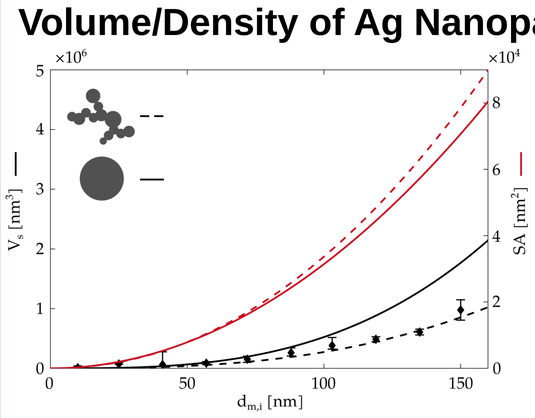


Figure 8: True volume (V_s) and surface area (SA) of Ag aggregates and spheres v. initial mobility diameter ($d_{m,i}$).

- Relationship between V_s and $d_{m,i}$ for Ag aggregates is
  $$V_s = 3.75\, d_{m,i}^{2.48}$$
- Average true density of Ag aggregates is obtained from the slope of the (m_i, V_s) curve and can reach down to ~ 2,000 kg/m^3, which agrees with the density found for Ag primary particles[5]
- Large overestimation of volume using spherical approximation
- Surface area is derived using the true volume according to semi-empirical relations[6]
- Size-dependent packing factor: 0.47 (135 nm) to 0.89 (57 nm)
- Size-dependent porosity is estimated using the effective density (from mass-mobility): 54% (135 nm) to 11% (57 nm)

- Small sintered Ag aggregates have also been measured: V_s = 1.4.10^3 nm^3 (20 nm), 6.2.10^3 nm^3 (30 nm), 7.9.10^3 nm^3 (40 nm). The retrieved density (~ 11,000 kg/m^3) is higher than both the oxidized and pure states of silver possibly due to changes in lattice parameter during sintering

Feasibility of a Coagulation Technique

Principles and Setup

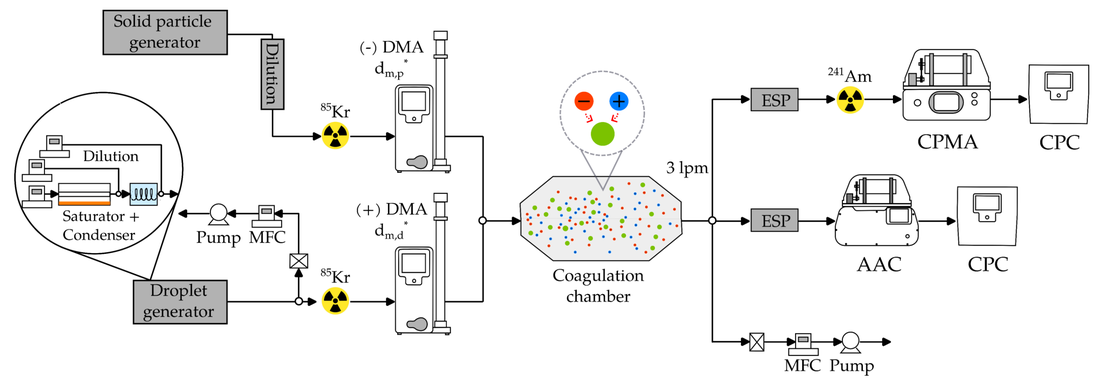


Figure 9: Coagulation rig.

Particle-Droplet Collision

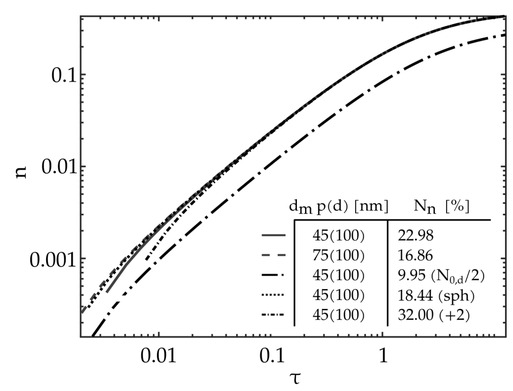


Figure 10: Modeled non-dimensional collision kernel components.

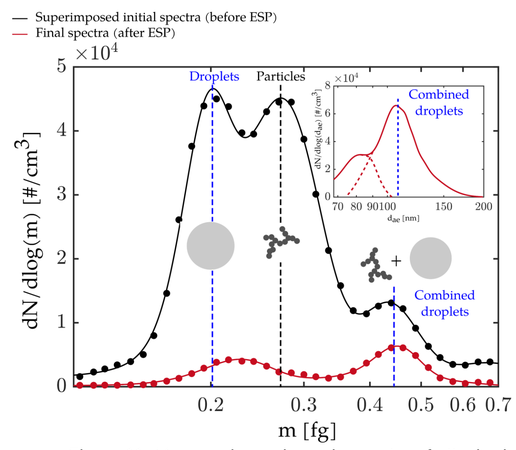


Figure 11: Mass and aerodynamic spectra of attached particles-droplets.

- 0-D collision model used to design the coagulation chamber and choose the experimental setpoints
- Mono-mobile droplets and particles shown to 'attach' via joint electrostatic and Brownian interactions
- Sticking coefficient assumed unity, however the collision v. coagulation kinetics need further investigation

References

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